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Sea shell derived adsorbent and its potential for treating acid mine drainage

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ABSTRACT

Acid mine drainage (AMD) treatment remains a virgin area for extensive research owing to the limitations of the existing and proposed AMD treatment technologies. Hence, the current study aims to apply crushed sea shells as an efficient and cost effective adsorption medium for AMD treatment in batch and column studies. The metal–adsorption medium interaction was characterized using FTIR and XRF analyses. The effects of adsorbent mass and solution pH were investigated in batch studies whilst initial concentration, flow rate and adsorbent bed mass were considered during fixed bed column studies. A close analysis of all parameters varied showed that initial metal concentration had the greatest effect on metal removal from AMD, with lower initial concentration resulting in more water being treated at breakthrough point. The experimental breakthrough curves for the removal of iron from AMD were fully described by the Yoon-Nelson and Thomas models. The preliminary results showed that sea shell derived adsorbent has a great potential as an alternative low cost material in the treatment of AMD.

1. Introduction

Acid mine drainage (AMD) is an environmental problem that has drawn the attention of researchers in several countries around the world. This is mainly due to the presence of heavy metals in AMD whose negative effects on the environment are well documented. For example, the percolation of AMD into the ground could lead to degradation of both surface and ground water making it unfit for human and animal consumption or crop irrigation. Sangita et al. (2010) noted that heavy metals in AMD are serious pollutants that can easily reach lakes, dams and rivers that are sources of water supply. For example, in South Africa the situation is exacerbated by the fact that most of the population, particularly those residing in rural communities use groundwater for drinking purposes (Masukume et al., 2011). To prevent or reduce the risk of groundwater contamination, there is an urgent need for acid mine drainage treatment. A lot of work has been done geared towards AMD treatment by different processes. Several methods such as chemical precipitation (Matlock et al., 2002; Maree et al., 2005; Hammarstrom et al., 2003; Bologo et al., 2012), ion exchange (Pollio and Kunin, 1967; Gaikwad et al., 2010), reverse osmosis (Zhang et al., 2007) and biological methods (Chang et al., 2000; Foucher et al., 2001) have been developed to treat AMD. However, these technologies are reported to be expensive, inefficient or environmentally unfriendly. In contrast, adsorption is one of the preferred technologies in water treatment due to its inherent features such as simplicity, environmental benignity and the availability of a wide range of adsorbents (Ghaedi et al., 2006).

Adsorption has been explored for heavy metal removal from wastewater (Rios et al., 2008). Onyango et al. (2007) noted that the success of adsorption technology depends on the performance of the chosen adsorbents and reliable supply of materials for the process. Li and Hong further argued that popular adsorbents such as activated carbon are not economically viable on a sustainable basis and are technically inefficient. Rios et al. (2008) concurred when he noted that activated carbon's production costs are quite high. Other adsorbents such as zeolites have also been widely used as adsorbent of heavy metals due to their metal binding capacity (Erdem et al., 2004; Salam et al., 2011) and ready availability; the low removal efficiency has, however, limited their application on a larger scale. The aforementioned disadvantages of conventional adsorbents warrant the need to search for alternative adsorbents that are readily available and show good metal removal capacities.

Consequently, in this study sea shell was used as an adsorbent for AMD treatment. Sea shell is a hard material in which the main constituent is calcium carbonate, which may assume either of two principal crystalline forms; calcite or aragonite (Narayanan et al., 2006). According to Garels, as reported by Tudor et al. (2006), sea shells adsorb metals such as Mn^{2+} via chemisorptions. Zachara et al. (1988) concluded that the adsorption of Zn^{2+} and Co^{2+} onto sea shells proceeded via ion-exchange with Ca^{2+}. Use of sea shells as adsorbents is economically and technically feasible owing to their low cost and being plentiful in nature and the material having intrinsic pore structures to entrap contaminants. The

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objective of the study was to investigate and explore the feasibility of using sea shell for the treatment of AMD. The adsorbent performance was considered for both batch and column studies. To the best of our knowledge there is hardly any information in the literature on the application of sea shells for AMD treatment.

2. Materials and methods

2.1. Acid mine drainage water samples

Samples of AMD used in this study were collected from the Rand Uranium Mine, Randfontein, South Africa. The water samples were collected in washed high density polyethylene (HDPE) containers sealed with air tight lids. The samples brought to the laboratory were filtered to remove particulates and then refrigerated at 4 °C prior to analysis. The metal concentrations in the samples were determined using the inductively coupled plasma optical emission spectroscopy (Spectro Arcos, Germany), whilst the anions were determined by column chromatography using a Metrosep A ion chromatograph. The sample pH was measured in the laboratory. Table 1 shows the concentrations of ions in AMD used in this study.

2.2. Adsorbent collection and preparation

The sea shells were collected from beaches near Cape Town, South Africa. The shells were thoroughly washed with deionized water to remove sand and other particles. The sea shells were then oven dried at 100 °C overnight. The dried shells were crushed and sieved into the following particle size ranges: <150 μm, 150–300 μm and 300–425 μm. Finally, the dried material was used for characterization and adsorption tests.

2.3. Adsorbent characterization

Fourier transform infrared spectroscopy (FTIR) was undertaken on a Perkin Elmer Spectrum 100 spectrophotometer. The FTIR spectra were recorded in the region of 500–4000 cm^{-1} with a spectra resolution of 4 cm^{-1}. The FTIR analysis of the adsorbent before and after adsorption is important to give an indication of whether adsorption proceeds by chemical or physical means. FTIR spectroscopy helps also to identify functional groups on the adsorbent surface that may be responsible for adsorption of contaminants from wastewater. In addition, the chemical composition of the adsorbent before and after adsorption was determined using the X-ray fluorescence (XRF). The adsorbent material was mixed with lithium nitrate, heated to 1000 °C, and then melt cast in a dish to produce a homogeneous glass-like bead. XRF results were obtained on an ARL 9400 XRF spectrophotometer and the results were processed using the Quantas software.

2.4. Batch adsorption experiments

Batch equilibrium experiments were carried out to investigate the performance of the sea shell adsorbent in treating AMD under different conditions. For adsorbent dosage as a variable, a weighed amount of sea shell (0.1–1.0 g) was contacted with 50 mL of AMD in a 100 mL plastic bottle. The sealed bottles were placed in a thermostatically controlled shaker operated at 150 rpm for 24 h at 25 °C. After 24 h, the samples were filtered through a Whatman Filter Paper No. 41 and the filtrate was analysed for residual iron, manganese, aluminium and sulphate concentrations. In a second set of experiments, the effect of pH on metal removal from AMD was explored by varying the initial solution pH from 1.7 to 4.8. Since AMD pH fluctuates with time owing to poor buffering and varies from source to source, it was imperative to study the effect of pH on metal removal from AMD. Solution pH has a significant effect on metal uptake, since it determines the surface charge of the adsorbent and the degree of ionization and speciation of the adsorbate (Yao et al., 2010). Adsorbent particle sizes of between 150 and 300 μm were utilized during batch studies.

Table 1
Chemical composition of AMD used in this study.

Parameter	Concentration
pH	2.3
Fe	425.4
Mn	81.8
Ni	1.8
Pb	0.6
Al	86.5
SO_4^{2-}	2564

All ions are in mg L^{-1} except the pH.

2.5. Fixed bed column experiments

Column experiments were performed using polyvinyl chloride (PVC) columns of 30 cm length and 20 mm internal diameter. AMD was fed into the column at a constant flow-rate, using a peristaltic pump in up-flow mode for complete wetting of the adsorbent particles. The flow-rate was checked periodically. The effect of process variables was explored as described below:

2.5.1. Effects of adsorbent bed mass

Real AMD was pumped through columns containing different masses of 30, 60 and 90 g of sea shell adsorbent, at a flow-rate of 5 mL min^{-1}. Initial metal concentrations and solution pH were maintained constant in all cases. The effluent samples were collected at given time intervals and analysed for metals using the ICP-OES spectrophotometer.

2.5.2. Effect of flow-rate

AMD was pumped in an upflow mode at a flow-rate of 2.5, 5.0 and 7.5 mL min^{-1} through columns packed with 60 g of sea shell. The initial metal concentrations and solution pH were kept constant. Effluent collection and metal analysis were done as described above.

2.5.3. Effect of initial concentration

The influence of initial metal concentration was assessed by varying initial metal concentrations in actual AMD between 36.96 to 81.8 mg L^{-1} and 233.22 to 425.4 mg L^{-1} for manganese and iron, respectively. The mass of sea shell was kept constant at 60 g whilst contaminated water was pumped at a constant flow-rate of 5 mL min^{-1} through the column. The solution was adjusted and maintained at pH 2.3 in all cases.

2.6. Performance indicators

In water treatment, fixed beds are usually operated with an objective to lower the concentration of a given contaminant to a value below the maximum allowable concentration. For a given adsorbent bed mass, the adsorption performance is directly related to the number of bed volumes processed before the breakthrough point is reached (Bhaumik et al., 2013). The number of bed volumes treated before breakthrough is given by Eq. (1):

$$Number\ of\ bed\ volumes(BV) = \frac{volume\ of\ water\ treated\ at\ breakthrough\ po\text{int}\ (L)}{volume\ of\ adsorbent\ bed(L)} \tag{1}$$

Moreover, the rate at which the adsorbent is exhausted during adsorption may be used to determine the regularity at which the